

Exact Generalization of Local Thermodynamics of Inhomogeneous Fluids to Arbitrary Spatial Scales

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In order to provide a formally correct thermodynamical description of inhomogeneous fluids valid on all length scales down to the classical limit we postulate that all extensive quantities have locally extensive analogues. We derive local thermodynamic relations for the canonical and isothermal-isobaric ensembles without limitations with respect to the nature of intermolecular interactions. The inhomogeneity of the system is shown to result in two distinct entropic contributions. The *intrinsic* contribution is due the specific distribution of local environments experienced by a single molecule while the *extrinsic* one originates exclusively from the local variation of the density from its bulk value. As an example the theory is applied to the surface tension of a spherical liquid droplet.

The study of spatially inhomogeneous fluids is important for a vast variety of applications, ranging from macroscopic surface and interfacial phenomena [1], spatially confined systems such as fluids confined to channels of porous materials [2], down to molecular solvation phenomena [3]. A proper theoretical framework for addressing these problems should be capable to unambiguously describe local thermodynamical properties. The term 'local' is to be understood in terms of a function that is well defined at a certain point in space and in general also depends on the state of the system in the neighborhood of the point. The size of the neighborhood as well as the spatial scale, on which the description is valid, depend critically on the level of theory.

Various theoretical attempts to describe 'local' thermodynamic properties of inhomogeneous fluids have been proposed (traditionally called *point thermodynamics*) relying either on Kirkwoods integral equation [4], spatially-dependent cluster expansions [5] or a density functional treatment [6]. In the first two approaches [4, 5] the definition of local thermodynamic potentials necessitates postulating the existence of a local pressure, which is justified on spatial scales, on which local properties vary slowly, but it fails on smaller scales, on which one has to introduce a pressure tensor due to spatial inhomogeneity [6]. A proper description which enables a full coupling of local thermal and mechanical properties was made using the density functional formalism [6]. While it consistently describes fluids near interfaces or confined in pores and also enables a direct extension to the description of transport of dense inhomogeneous fluids it builds on the assumption that the correlation function is short ranged [7]. Thus it cannot be applied to describe systems on the scale of the correlation length or even below, such as of immediate interest, for example, in solvation phenomena [3] or molecules confined to nanotubes [8]. In these systems one is often specifically interested in entropic effects (*i.e.* the constraining of molecular degrees of freedom). Inevitably one has to resort to some sort of correlation

expansion [9], which becomes impractical for inhomogeneous systems and is therefore usually *ad hoc* truncated at the pair correlation level. As significant higher order correlations were found already in homogeneous simple liquids [10] such a truncation can not be appropriate in the case of hydration [11]. More importantly, the use of thermodynamic concepts in the case when the dimension of the studied (sub)system is comparable to or smaller than the correlation length, is formally not justified. The immediate technological interest in such systems such as nanofluidic applications [12] and wetting phenomena in nanotubes [13], poses a pressing need for a general formulation of local thermodynamics on such small length scales. At present, such a formal framework is still elusive and even the question of mere validity of thermodynamical concepts on spatial scales comparable to or smaller than the correlation length is still under debate.

Here we present an exact rigorous formulation of local thermodynamics of inhomogeneous fluids at equilibrium, which holds on arbitrary spatial scales down to the classical limit without any limitations regarding intermolecular interactions or the origin of the inhomogeneity. Based on the test particle picture we show that the specification of the order of correlations can be entirely avoided while they are inherently built into the theory. Defining locally extensive properties we derive a complete set of local thermodynamic relations in the canonical and isothermal-isobaric ensemble. An exact expression for the surface tension of a spherical liquid droplet is derived as a 'proof of concept' example. Finally, we discuss the physical meaning of local thermodynamic potentials on scales smaller than the correlation length.

While the quantities pertaining to properties of single molecules (e.g. local density, $\langle \rho(\mathbf{r}) \rangle$) have an unambiguous local definition, functions which are averages over the properties of larger groups of molecules (e.g. free energy density, $f(\mathbf{r})$, or entropy density, $s(\mathbf{r})$), cannot be unambiguously defined but are required to fulfill certain constraints, typically the invariance of some of the lower moments of the functions [1]. We postulate that all nominally extensive quantities have well defined local analogues and therefore introduce the notion of a *locally*

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extensive quantity $a(\mathbf{r})$ as:

$$a(\mathbf{r}) \equiv \langle \rho(\mathbf{r}) \rangle A^1(\mathbf{r}), \quad (1)$$

where the superscript 1 denotes the property per single molecule located in the volume element $d\mathbf{r}$ centered in \mathbf{r} . We describe the 'per molecule' or 'quasi-single' particle property within the test particle-insertion picture, where a local quantity is typically a function of the insertion energy of the *virtual* test molecule and assign the entire potential energy change to the test molecule. We show that such a choice leads to invariant values of integrals of local thermodynamic functions over space. We focus on excess thermodynamic properties since the corresponding ideal contributions are trivial to evaluate.

In the canonical ensemble we begin by defining $f_{ex}(\mathbf{r})$ in terms of the excess free energy per molecule located in the differential volume element, $\overline{F}_{ex}^1(\mathbf{r})$, which can be understood as the change in excess free energy upon insertion of an additional molecule at position \mathbf{r} at constant T and V integrated over all orientations of the inserted molecule and all configurations (positions as well as orientations) of the remaining N molecules. $\overline{F}_{ex}^1(\mathbf{r})$ is expressed in terms of the corresponding configurational integrals of the $(N+1)$ - and N -particle systems: $\overline{F}_{ex}^1(\mathbf{r}) = -k_B T \ln \frac{Z_{N+1}(\mathbf{r})}{Z_N}$. We denote the intermolecular interaction energy of the N molecules as U_N and the interaction energy of these molecules with the external field (the potential due to the presence of the solvent) as ψ_N . The potential energy of the inserted $(N+1)$ -st molecule, including both the interactions with the remaining N molecules and the interaction with the external field, is denoted as φ . Thus, the potential energies read $U_N + \psi_N$ and $\varphi + U_N + \psi_N = U_{N+1} + \psi_{N+1}$ in the N and $(N+1)$ system, respectively. The configuration of the i -th water molecule is specified by stating its position and orientation, $\mathbf{s}_i = (\mathbf{r}_i, \Omega_i)$. Written out explicitly, $f_{ex}(\mathbf{r})$ reads:

$$f_{ex}(\mathbf{r}) = -\beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \left\langle \int d\Omega \exp(-\beta\varphi(\mathbf{r}, \Omega)) \right\rangle_N, \quad (2)$$

where $\beta = 1/k_B T$ and the subscript N denotes the average over all configurations of the remaining N molecules. In the case where the system is homogeneous (denoted with index 0) Eq. (2) reduces to the bulk density multiplied by $\overline{F}_{ex,0}^1$, the latter term being equal to Widom's formula for the excess chemical potential $\rho_B \overline{F}_{ex,0}^1 \equiv \rho_B \mu_{ex}$. In the case where the external potential, $\psi(\mathbf{r})$, is spherically symmetric, Eq. (2) splits into an external field contribution, $\langle \rho(\mathbf{r}) \rangle \psi(\mathbf{r})$, and an intrinsic term, $-\beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \langle \int d\Omega \exp(-\beta u(\mathbf{r}, \Omega)) \rangle_N$, with $\psi = \psi_{N+1} - \psi_N$ and $u = U_{N+1} - U_N$. This separation establishes a connection with density functional theory (DFT) and the Yvon-Born-Green hierarchy. Namely, it is known that the chemical potential of an inhomogeneous system splits into the intrinsic chemical potential, μ_{int} , and the external field contribution, *i.e.*

$\mu = \mu_{int}(\mathbf{r}) + \psi(\mathbf{r})$. Explicitly, $\mu_{int}(\mathbf{r})$ is the functional derivative of the intrinsic free energy functional [1, 14], $\frac{\delta F_{int}[\rho]}{\delta \langle \rho(\mathbf{r}) \rangle} = \mu_{int}(\mathbf{r})$. The intrinsic free energy functional can be divided into ideal and excess parts and the latter can be identified formally as the excess intrinsic chemical potential, $\mu_{int}^{ex}(\mathbf{r}) = \frac{\delta F_{int}^{ex}[\rho]}{\delta \langle \rho(\mathbf{r}) \rangle}$ (see for example [1, 14]) or equivalently the singlet direct correlation function, $c^1(\mathbf{r})$ in integral equation theories and the Yvon-Born-Green hierarchy [1, 14, 15]. Note that if instead we had $\psi = \psi(\mathbf{r}, \Omega)$ a DFT free energy functional would read $F_{ex} = \int d\mathbf{r} \int d\Omega \langle \rho(\mathbf{r}, \Omega) \rangle_N \overline{F}_{ex}^1(\mathbf{r}, \Omega)$. A factorization of the chemical potential into intrinsic and external contributions as to be used in a DFT-like approach would then be rather useless. Meanwhile a generalization of the first member of the YBG hierarchy can in fact be obtained formally by using the invariance of the system under simultaneous rotation of the molecules and the coordinate system [16].

The excess entropy density, s_{ex} , is obtained from the thermodynamic identity $S_{ex} = -\frac{\partial F_{ex}}{\partial T}$. Taking the partial derivative inside the integral and using the subscript Ω and a shorthand notation for the angular integration, $\langle \dots \rangle_\Omega = \int \dots d\Omega$ we obtain $S_{ex} = -\int \frac{\partial}{\partial T} f_{ex}(\mathbf{r}) d\mathbf{r} \equiv \int s_{ex}(\mathbf{r}) d\mathbf{r}$ or explicitly

$$s_{ex}(\mathbf{r}) = \frac{1}{T} \left(\beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \langle \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_N - \ln \langle \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_N \frac{\partial}{\partial \beta} \langle \rho(\mathbf{r}) \rangle_N - \langle \rho(\mathbf{r}) \rangle \frac{\partial}{\partial \beta} \ln \langle \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_N \right). \quad (3)$$

The first and third terms in Eq. (3) represent the contribution of *intrinsic* excess entropy of single molecules, $\overline{S}_{ex}^1(\mathbf{r}) \equiv -\frac{\partial \overline{F}_{ex}^1(\mathbf{r})}{\partial T}$, and expresses the number of degrees of freedom of single molecules at \mathbf{r} , while the second term can be understood as an *extrinsic* excess entropy density, $-\overline{F}_{ex}^1(\mathbf{r}) \frac{\partial \langle \rho(\mathbf{r}) \rangle}{\partial T}$, and is solely due to the fact that the system is inhomogeneous (it is zero for a homogeneous system). Due to the indistinguishability of molecules the local density can be written as $\langle \rho(\mathbf{r}) \rangle = \langle \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \rangle \equiv N \langle \delta(\mathbf{r}_1 - \mathbf{r}) \rangle$, and we obtain after straightforward algebra that

$$\frac{\partial}{\partial \beta} \langle \rho(\mathbf{r}) \rangle = \langle \rho(\mathbf{r}) \rangle \langle W_N \rangle_N - N \langle W_N \delta(\mathbf{r}_1 - \mathbf{r}) \rangle_N. \quad (4)$$

with $W_N = U_N + \psi_N$. Eq. (4) gives a vanishing change in particle number when integrated over the volume as it should (since we work in the (N, V, T) ensemble). By defining the average in the N -particle ensemble where molecule 1 is fixed at \mathbf{r} (or equivalently, an average over all configurations in which one of the molecules is located at \mathbf{r}) as

$$\langle \mathcal{O} \rangle_N^r = \frac{\langle \mathcal{O} \delta(\mathbf{r}_1 - \mathbf{r}) \rangle_N}{\langle \delta(\mathbf{r}_1 - \mathbf{r}) \rangle_N} \equiv \frac{\langle \mathcal{O} \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_{N-1}}{\langle \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_{N-1}}, \quad (5)$$

we find that the following relation holds

$$\frac{\partial}{\partial \beta} \langle \rho(\mathbf{r}) \rangle = \langle \rho(\mathbf{r}) \rangle (\langle W_N \rangle_N - \langle W_N \rangle_N^r), \quad (6)$$

Eq. (6) expresses the fact that the change of local density with temperature depends on the difference between the potential energy of the system and the average energy of configurations where one molecule is fixed at \mathbf{r} . Eq. (6) tells us that the local density will decrease with increasing temperature if the average energy of configurations with one molecule fixed at \mathbf{r} is more favorable than the potential energy of the system. It indicates that a locally increased density with respect to the bulk density (*i.e.* the density sufficiently far away from the source of the perturbation) is disfavored in terms of the excess entropy as it naturally decreases the configurational volume in phase space. Elementary algebraic manipulations give the following expression for the intrinsic excess entropy per molecule

$$\overline{S}_{ex}^{intr,1}(\mathbf{r}) = k_B \ln \langle \exp(-\beta \varphi(\mathbf{r}, \Omega)) \rangle_N + \frac{\langle W \rangle_{N+1}^r - \langle W \rangle_N}{T} \quad (7)$$

where we have dropped the index for the potential energy indicating the number of molecules involved as it is equal to the one denoting the ensemble average. Using Eqns.(6) and (7) Eq. (3) can be rewritten in the final form

$$s_{ex}(\mathbf{r}) = \frac{1}{T} \langle \rho(\mathbf{r}) \rangle \left(\ln \langle \exp(-\beta \varphi(\mathbf{r}, \Omega)) \rangle_N \times \{ \beta^{-1} + \langle W \rangle_N^r - \langle W \rangle_N \} + \langle W \rangle_{N+1}^r - \langle W \rangle_N \right). \quad (8)$$

Here, using $E = F + TS$, the expression for the excess energy density, $e_{ex}(\mathbf{r})$, can be trivially written as:

$$e_{ex}(\mathbf{r}) = \langle \rho(\mathbf{r}) \rangle \left(\ln \langle \exp(-\beta \varphi(\mathbf{r}, \Omega)) \rangle_N \{ \langle W \rangle_N^r - \langle W \rangle_N \} + \langle W \rangle_{N+1}^r - \langle W \rangle_N \right). \quad (9)$$

Eqns. (2), (8) and (9) represent the fundamental local equations for the canonical ensemble. We see that the nominally extensive property exactly generalizes to the locally extensive property for inhomogeneous systems. The local equations contain an intrinsic ('per single molecule') part and an additional extrinsic contribution, $\langle \rho(\mathbf{r}) \rangle \ln \langle \exp(-\beta \varphi(\mathbf{r}, \Omega)) \rangle_N \frac{\langle W \rangle_N^r - \langle W \rangle_N}{T}$, due to the inhomogeneity of the system. The extrinsic component expresses the energy *redistribution*. It is caused by a local density change with respect to a homogeneous system due to the redistribution of molecular positions at given local density of energy states per molecule. The intrinsic part reflects the local density of energy states per molecule and the change of potential energy of the system when a molecule is added to the ensemble at the specified position. We deliberately avoid defining the local pV term, as the scale-independent definition of the local work is *ad hoc* not possible because of its inherent

non-local nature. However, we show in the following that the appropriate local pV analogue arises naturally in the (N, p, T) ensemble.

Analogous to the (N, V, T) ensemble we again assume that the Gibbs free energy density is locally extensive, $g_{ex}(\mathbf{r}) \equiv \overline{G}_{ex}^1(\mathbf{r}) \langle \rho(\mathbf{r}) \rangle$, where $\overline{G}_{ex}^1(\mathbf{r})$ is the excess Gibbs free energy per molecule located in the differential volume element and $\langle \rho(\mathbf{r}) \rangle = \langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \rangle$ is the local density (at constant N, p and T) in the presence of an external field ψ . The total Gibbs free energy per molecule located in the differential volume element centered at \mathbf{r} is defined in terms of the configurational isothermal-isobaric partition functions of the N and $N+1$ systems: $\overline{G}_c^1(\mathbf{r}) = -k_B T \ln \frac{\Delta_{N+1}(\mathbf{r})}{\Delta_N}$ [17]. The excess Gibbs free energy density can be written as,

$$g_{ex}(\mathbf{r}) = -\beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \frac{\langle V \int d\Omega \exp(-\beta \varphi(\mathbf{r}, \Omega)) \rangle_N}{\langle V \rangle_N}, \quad (10)$$

In the limit of small volume fluctuations, $\Delta V/V \rightarrow 0$, the volume terms cancel each other and Eq.(10) reduces to Eq.(2). The fluctuating volume term will be important where volume fluctuations are expected to be large. Important examples include dewetting phenomena of meso- and macroscopic surfaces [18, 19], hydrophobicity on the mesoscale [20] and dewetting transitions in nanochannels [21].

The factorization of $g_{ex}(\mathbf{r})$ into excess enthalpy density, $h_{ex}(\mathbf{r})$, and $s_{ex}(\mathbf{r})$ can be achieved by introducing the average volume $\langle V \rangle_{N+1}^r$ in a $(N+1)$ -particle ensemble in which the $(N+1)$ -st molecule position is fixed at \mathbf{r} using Eq. (5):

$$g_{ex}(\mathbf{r}) = -\beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \langle \exp(-\beta \varphi(\mathbf{r})) \rangle_N - \beta^{-1} \langle \rho(\mathbf{r}) \rangle \ln \frac{\langle V \rangle_{N+1}^r}{\langle V \rangle_N}, \quad (11)$$

where the first term is recognized as the (Helmholtz) free energy density and the second term reflects the relative response of the system volume to the insertion of an additional molecule at a point \mathbf{r} given fixed T and p . Comparing Eq. (11) with the relation between the Gibbs and Helmholtz free energies we recognize that the second term in Eq. (11) is the exact local analogue of the pV term and immediately demonstrates the fact that the work is intrinsically performed non-locally. At the same time it also demonstrates that the total work has a well defined local contribution, which is exactly locally extensive. $h_{ex}(\mathbf{r})$ is obtained directly as $g_{ex}(\mathbf{r}) + T s_{ex}(\mathbf{r})$ and all three together constitute the exact fundamental local relation for the isothermal-isobaric ensemble.

Meanwhile, the chemical potential is strictly constant throughout the system and can only artificially be given a local physical interpretation, $\mu_{ex} = \int \mu_{ex}^{loc}(\mathbf{r}) d\mathbf{r}$, in terms of an average contribution per molecule $\mu_{ex} = N^{-1} \int g_{ex}(\mathbf{r}) d\mathbf{r}$.

The locally-extensive formulation of statistical thermodynamics reduces to the standard description in case of

a homogeneous system. On the other hand it must also reduce to the classical bulk thermodynamic formulation upon spatial integration. By noting that the Helmholtz free energy is related to μ via $F = N\mu - pV \equiv N\phi$, where ϕ is the (Helmholtz) free energy per molecule. Recalling that the ideal gas contribution to F in the inhomogeneous local picture is $F_{id} = \beta^{-1} \int \langle \rho(\mathbf{r}) \rangle (\ln \langle \rho(\mathbf{r}) \rangle - 1) d\mathbf{r}$ we obtain for $F = F_{id} + F_{ex}$, disregarding kinetic terms, $\beta^{-1} \int \langle \rho(\mathbf{r}) \rangle \ln [\langle \rho(\mathbf{r}) \rangle / \langle \exp(-\beta\varphi(\mathbf{r}, \Omega)) \rangle_N] d\mathbf{r}$. According to the potential distribution theorem [22] the logarithmic term is constant, leading to $F = N\phi$, as expected. However, this suggests that Widom's definition of the chemical potential for an inhomogeneous system (within the framework of the potential distribution theory)[22] is in fact the free energy per particle. Clearly, for $N \rightarrow \infty$, μ and ϕ become equivalent.

As a case study we present an exact derivation of the surface tension of a single component liquid droplet in absence of external fields such that the liquid/gas interface is on average spherical. Addressing this problem in the framework of statistical mechanics using either mechanical or point thermodynamical approaches is known to introduce a degree of arbitrariness into the problem such that the surface of tension (the surface in which the tension acts) is said to be ill-defined [1]. For notational convenience we assume that intermolecular interactions are spherically symmetrical but may include many-body contributions of arbitrary order. The system contains internal liquid (l) and external gaseous (g) bulk phases separated by a non-uniform interfacial region (s). Choosing the radius of the dividing surface, r_s , determines the volumes of the bulk phases $V = V_l + V_g$. Constancy of total number of molecules demands $N = N_l + N_g + N_s = 4\pi \int r^2 \langle \rho(r) \rangle dr$. Only excess quantities contribute to the surface tension and F_{ex} of the system can be written in terms of bulk and surface contributions $F = F_l + F_g + F_s$. Depending on r_s the values of N_s and F_s can formally be positive or negative. By definition the surface tension, σ , represents the excess free energy of the dividing surface per unit of its area: $\sigma = (4\pi r_s^2)^{-1} (F - (F_g + F_l))$. Extensivity, $F_{l(g)} = N_{l(g)} \overline{F}_{ex,0}^{1;l(g)}$ (where the subscript 0 denotes the homogeneous N -molecule ensemble of bulk phase $l(g)$ at the same T and V), allows us to write

$$\sigma = r_s^{-2} \left\{ \int_0^{r_s} r^2 \langle \rho(r) \rangle \left(\overline{F}_{ex}^l(r) - \overline{F}_{ex,0}^{1;l} \right) dr + \int_{r_s}^{\infty} r^2 \langle \rho(r) \rangle \left(\overline{F}_{ex}^l(r) - \overline{F}_{ex,0}^{1;g} \right) dr \right\}. \quad (12)$$

We have $\sigma = \sigma(r_s)$ and it is known that at the actual surface of tension the formal derivative vanishes at r_t ,

$d\sigma/dr_s|_{r_s=r_t} = 0$ [1]. Applying the chain rule and making use of the second fundamental theorem of calculus we can perform the derivation and obtain an implicit equation for r_t :

$$\frac{r_t^3}{2} \langle \rho(r_t) \rangle (\overline{F}_{ex}^{1;g} - \overline{F}_{ex}^{1;l}) = \int_0^{r_t} r^2 \langle \rho(r) \rangle \vartheta^l(r) dr + \int_{r_t}^{\infty} r^2 \langle \rho(r) \rangle \vartheta^g(r) dr, \quad (13)$$

where $\vartheta^{l(g)}(r) = \ln \frac{\exp(-\beta\overline{F}_{ex,0}^{1;l(g)})}{\langle \exp(-\beta\varphi(r)) \rangle_N}$. Once we know $\langle \rho(r) \rangle$, $\overline{F}_{ex,0}^{1;l(g)}$ and $\langle \exp(-\beta\varphi(r)) \rangle_N$, all of which can be readily calculated from Monte Carlo or Molecular Dynamics simulations, we can compute the surface tension as

$$\sigma = \int_0^{r_t} \frac{r^2}{r_t^2} \langle \rho(r) \rangle \{ \vartheta^l(r) H(r_t - r) + \vartheta^g(r) H(r - r_t) \} dr, \quad (14)$$

where $H(x)$ denotes the Heaviside function. Analogous equations are obtained in the case of a flat interface, where the surface of tension is chosen such as to satisfy $N_s = 0$. Eqs. (12) and (14) show that the *local density of surface free energy*, (local density of σA), is also exactly locally extensive. The above derivation can be viewed as the exact accomplishment of the van der Waals original approximate program for flat interfaces based on point-thermodynamics [1, 23]. The present method is free of arbitrariness and avoids the use of local pressure tensors, which are known to be non-uniquely defined [1].

In this letter we propose an exact general formulation of local thermodynamics of inhomogeneous fluids in the canonical and isothermal-isobaric ensembles, which is valid on all length scales without limitations with respect to nature intermolecular interactions. By introducing the notion of a *locally extensive quantity* we have shown that the thermodynamic potentials, which are inherently non-local, all have a well defined local physical meaning. Our results show that there are two distinct physical consequences of inhomogeneity, an *intrinsic* one due to the specific properties of the local environment giving rise to a specific local density of states of a molecule, and an *extrinsic* one, which is explicitly due to the inhomogeneous distribution of molecular positions throughout the system. The theory was used to derive an exact expression for the surface tension of a spherical liquid droplet. Our results pose the formal basis for a general local thermodynamic description of inhomogeneous fluids ranging from macroscopic interfacial phenomena, molecular solvation to such as encountered in modern nanofluidic devices.

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